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Short communication

A highly flexible polymer fibre battery

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Abstract

The development of highly flexible fibre batteries based on conducting polymers is described. The performance of cells with polypyrrole–hexafluorophosphate (PPy/PF_6) and polypyrrole–polystyrenesulfonate (PPy/PSS) is evaluated. Based on the results, fibre batteries consisting of a PPy/PF_6 cathode and a PPy/PSS anode are fabricated and tested in an electrolyte of 1 M $LiPF_6$ in a mixture of ethylene carbonate and dimethyl carbonate. Capacities in the order of 10 mAh g^{-1} over 30 cycles were observed.

Keywords: Fibre battery; Conducting polymers; Electrochemical deposition; Polypyrrole; Capacity

1. Introduction

The integration of electronic components into conventional garments to introduce novel fashion effects, visual displays or audio and computing systems has generated interest in recent years [1,2]. Such systems are also proving useful in the development of wearable diagnostic systems for monitoring of vital data (heart, pulse rate) in medical and military applications.

The integration of sensors and actuators into fibres/textiles has also been of interest. The realisation of high efficiency, conducting polymer actuator fibres [3] and conducting polymer fibres with chemical sensing [4–6] or electrochromic [7] capabilities raises promising opportunities. Alternatively, conducting polymer coatings on textiles can function as chemical [8] or biomechanical [9] sensors, as wearable heating elements [10,11] or even as biocompatible materials for mammalian cell culturing [12].

The area of electronic textiles does, however, require wearable energy-storage capabilities. This has stimulated the development of fibre batteries based on the use of conducting polymers. A number of strategies have been adopted for the utilisation of conducting polymers as rechargeable battery devices [13,14]. Many studies have addressed the possibility of replacing either the negative (anode) or positive (cathode) electrode with a conducting polymer—more typically, the cathode because traditional metal anodes have significantly higher specific energies than polymers [15]. A more interesting possibility is the development of all-polymer batteries, where an electroactive polymer comprises both the anode and the cathode and is supported on an inert conducting support such as graphite or platinum. Killian et al. [16] reported the assembly of an all-polymer battery structure that used both p- and n-dopable polypyrrole with a specific charge capacity of 22 mAh g^{-1} at a cell potential of 0.4 V. The cells showed no loss in capacity when subjected to 100 cycles. The capacity was in fact much lower than that of the conventional lithium-ion battery, but all-polymer batteries have a potential advantage in that unique configurations can be devised and constructed. Of particular interest to us is the integration of all-polymer batteries into wearable or other textile-based structures. Consequently, this study is the first step towards the development of a flexible fibre battery construction, which uses a polypyrrole composite.

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2. Experimental

2.1. Electrode preparation and cell fabrication

All-polymer electrodes were fabricated by electropolymerization. The process was carried out using a three-electrode electrochemical cell. The potential required for polymerization was applied by means of a BAS CV-27 voltammograph.

2.1.1. Preparation of film electrodes and conventional cells

Stainless-steel mesh (Metal Mesh Pty Ltd., Australia) was used as the substrate for fabrication of the polypyrrole–hexafluorophosphate (PPy/PF_6) and polypyrrole–polystyrenesulfonate (PPy/PSS) film electrodes.

The PPy/PF_6 film was electrochemically prepared using solutions that contained 0.05 M tetrabutylammonium hexafluorophosphate and 0.06 M pyrrole in propylene carbonate (PC) at 0.75 V (versus Ag/Ag^+ in 0.01 M $AgNO_3$, 0.1 M tetrabutylammonium perchlorate (TBAP)/CH_3CN)). Following electropolymerization, the electrodes were dried in a vacuum oven for 24 h at room temperature, then cut to a small size of 1 cm^2 and transferred to an argon-filled glove box. The weight of polymer was about 2 mg. The dried electrodes were assembled into cells and tested.

The film of PPy/PSS was electropolymerized potentiostatically at 0.75 V (versus Ag/Ag^+, in 0.01 M $AgNO_3$, 0.1 M TBAP/CH_3CN) from 0.16 M pyrrole and 0.26 M polystyrene sulfonate (molar mass of 70,000 g mol^{-1}, Na^+ form, Aldrich) in a solvent mixture of distilled water and acetonitrile (3:1, v/v). After electropolymerization, the electrode for an all-polymer cell was converted into the fully reduced form by polarization at −1.3 V (versus Ag/Ag^+). The electrodes were dried and cut to a small size of 1 cm^2, and then stored in an argon-filled glove box. The weight of polymer was about 4 mg.

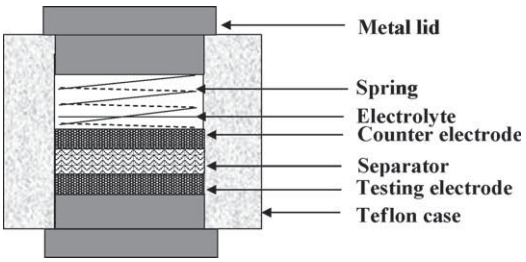


Fig. 1. Construction of conventional test cell.

The test cell consisted of two stainless-steel lids, a Teflon case and a spring, as shown schematically in Fig. 1. Lithium foil of 300 μm thickness and area of 1 cm^2 was used as the counter electrode. The electrolyte was 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v, provided by Merck KgaA, Germany). A polypropylene microporous separator was sandwiched between the two electrodes. Cells were assembled in an argon-filled glove box (Unilab, Mbraun, USA) in which both water and oxygen concentrations were kept below 5 ppm.

2.1.2. Preparation of fibre electrodes and fibre cells

Fine polypyrrole electrodes were fabricated by polymerization of pyrrole on to platinum wire with a diameter of 250 μm. The electropolymerization was carried out using a solution containing 0.06 M pyrrole and 0.05 M $TBAPF_6$ in PC at 0.75V (versus Ag/Ag^+ in 0.01 M $AgNO_3$, 0.1 M TBAP/CH_3CN). The electrodes were dried in a vacuum oven and stored in a glove box. The PPy/PF_6-coated Pt wire electrode is shown in Fig. 2A. The thickness of the PPy/PF_6 film

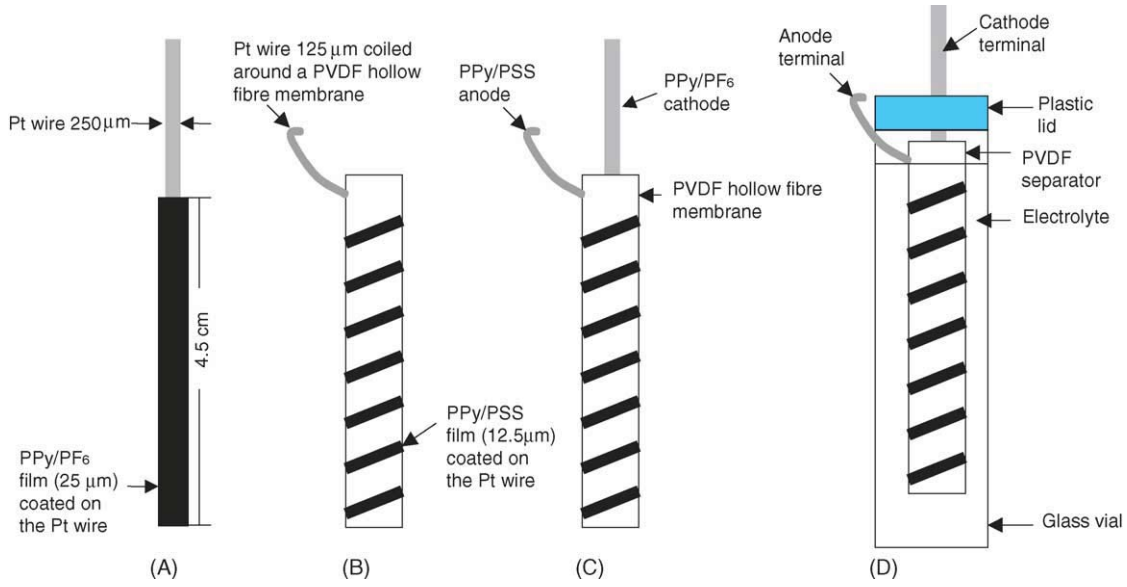


Fig. 2. Construction of hollow fibre composite cell. (A) PPy/PF_6-coated Pt wire electrode; (B) PPy/PSS-coated Pt wire around PVDF hollow fibre membrane; (C) PPy/PF_6 cathode electrode inserted into PPy/PSS-coated Pt wire–PVDF hollow fibre membrane composite anode; (D) schematic of fibre cell.

was about 25 μm, and the weight of active material (oxidized form) was about 1 mg.

PPy/PSS composite fibre electrodes were fabricated using a poly(vinylidene) fluoride (PVDF) hollow fibre membrane and a platinum wire (125 μm diameter). The internal and external diameters of the membrane were 0.7 and 1 mm, respectively, and the length was 4.5 cm. The Pt wire was wound tightly around the membrane (Fig. 2B). Polypyrrole–polystyrenesulfonate (PPy/PSS) was electropolymerized potentiostatically on to the platinum wire at 0.75 V (versus Ag/Ag^+, in 0.01 M $AgNO_3$, 0.1 M $TBAP/CH_3CN$) from 0.16 M pyrrole and 0.26 M polystyrenesulfonate (molar mass of 70,000 g mol^{-1}, Na^+ form, Aldrich) in a solvent mixture of distilled water and acetonitrile (3:1, v/v). After electropolymerization, the electrode was converted into the fully reduced form by polarization at −1.3 V (versus Ag/Ag^+). The PPy/PSS–PVDF hollow fibre composite electrode is shown in Fig. 2B. The thickness of the PPy/PSS film was 12.5 μm, and the weight of active material (reduced form) was about 1.5 mg.

A novel electrochemical fibre cell was then assembled in an argon-filled glove box. The oxidised form of PPy/PF_6 on the Pt wire (cathode) was inserted into the reduced form of PPy/PSS/Pt wire−PVDF hollow fibre composite (anode) (Fig. 2C). The PVDF hollow fibre had dual purposes: (i) to act as a support for the PPy/PSS/Pt wire and (ii) to function as a separator for the fibre battery. The two electrodes were put into a glass vial filled with an electrolyte of 1 M $LiPF_6$ in EC–DMC before the cell was sealed (Fig. 2D). Photographs of the PPy/PSS/Pt wire–PVDF hollow fibre composite anode (A), the PPy/PF_6-coated Pt wire cathode (B) and the assembled hollow fibre composite test cell (C) are shown in Fig. 3.

2.2. Cell tests

Charge–discharge testing was carried out using a battery-testing device (Neware, Electronic Co., China) interfaced to a computer that was loaded with suitable software. The battery testing system was capable of switching between charge and discharge automatically according to the pre-set cut-off potentials. The cells were tested at a constant current density of 0.1 mA cm^{-2}.

3. Results and discussion

Initially, the individual components (anode and cathode) of the fibre battery were tested independently. The PPy/PF_6-coated Pt wire electrode (Fig. 2A) and the PPy/PSS/Pt wire–PVDF hollow fibre membrane electrode (Fig. 2B) were tested separately in a lithium cell and compared to the performance observed with conventional polymer film electrodes. The oxidised form of PPy/PF_6 was used as the cathode and the reduced form of PPy/PSS was used as the anode. Therefore, PPy/PF_6 electrodes were cycled in a higher voltage range (2.5–4.2 V) in a lithium cell, whereas the PPy/PSS electrodes were cycled between 0–2 V.

The discharge curves obtained for the PPy/PF_6 electrode (10th cycle) are given in Fig. 4. As reported in previous publications for the polypyrrole-based cathode in a lithium cell [17–19], there are no obvious discharge plateaux for the cells with wire or film electrodes. The discharge capacity of the PPy/PF_6|Pt wire electrode cell is about 75 mAh g^{-1}, which is similar to that for a cell with a film PPy/PF_6 electrode (79 mAh g^{-1}).

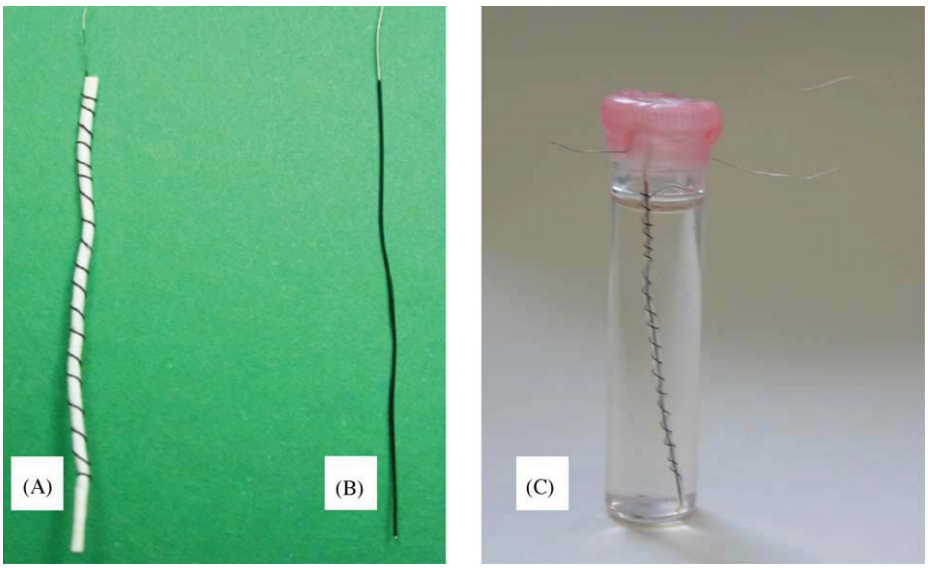


Fig. 3. Photographs of: (A) PPy/PSS/Pt wire–PVDF hollow fibre membrane composite anode; (B) PPy/PF_6-coated Pt wire cathode; (C) test cell of PPy/PF_6 wire|$LiPF_6$–EC–DMC|PPy/PSS–PVDF hollow fibre membrane composite.

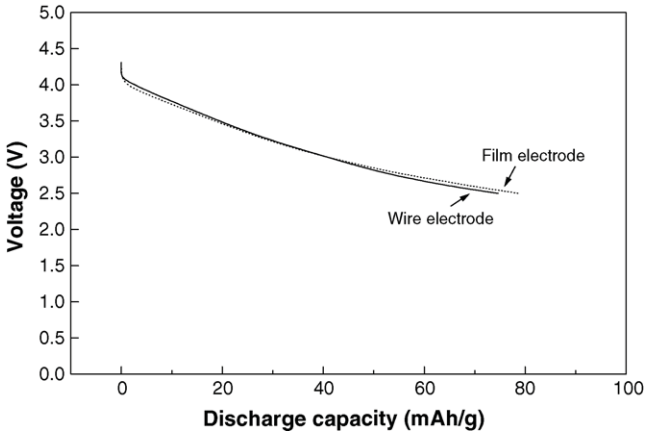


Fig. 4. Discharge curves obtained for PPy/PF6-coated Pt wire and film electrodes used as cathodes in lithium cell; current density = 0.1 mAh cm^{-2}.

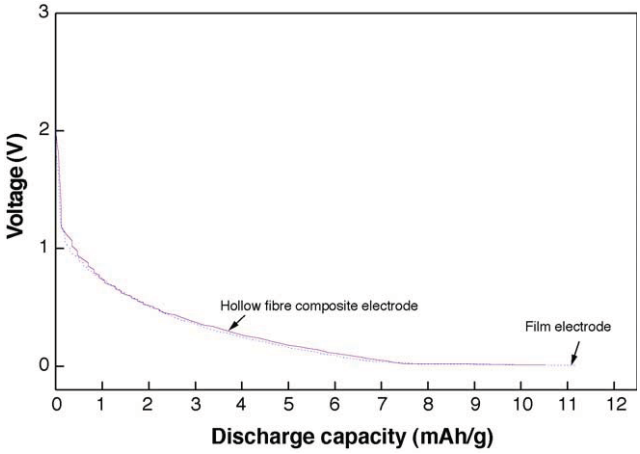


Fig. 5. Discharge curves obtained for PPy/PSS/Pt wire–PVDF hollow fibre membrane composite electrode and PPy/PSS film electrodes in lithium cells; current density = 0.1 mAh cm^{-2}.

Discharge curves were obtained for the PPy/PSS/Pt wire–PVDF hollow fibre membrane composite electrode and PPy/PSS film electrodes in a lithium cell (Fig. 5). The curves are similar for both cells, but the discharge capacity of the hollow fibre composite electrode is slightly lower than that of the film electrode. The discharge capacity of PPy/PSS electrodes is much lower than that of the PPy/PF_6 electrode because it was cycled within a lower potential range.

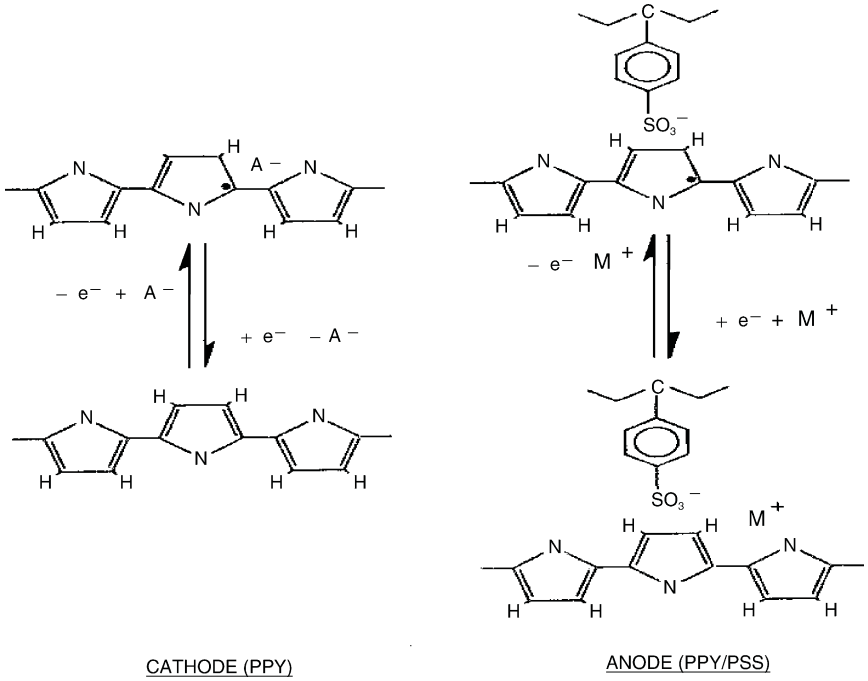
Polymer batteries using a conventional battery configuration and the novel hollow fibre membrane configuration were fabricated and tested. The batteries consist of a PPy/PF_6 cathode, a PPy/PSS anode and an electrolyte of 1 M $LiPF_6$ in an EC–DMC mixture. The capacity of the polymer batteries was based on the active mass of the anode.

The basis of the polymer battery operation is shown in Scheme 1 [16]. The cathode cycles between the oxidised, fully charged, condition of the conducting polymer, in which a charge-compensation anion intercalates to maintain charge neutrality ($A^- = PF_6^-$), and the neutral uncharged condition. The anode cycles between the neutral, fully charged, condition with a charge compensation intercalated cation ($M^+ = Li^+$) and the oxidised condition.

The reaction at the anode and cathode during discharge in a cell with $LiPF_6$ as the electrolyte can be represented as:

Anode:

$$[PPy^0/PSS^-]\,Li^+ \rightarrow [PPy^+/PSS^-] + Li^+ + e^- \qquad (1)$$



Scheme 1. Oxidation/reduction schemes for PPy–PPy/PSS system.

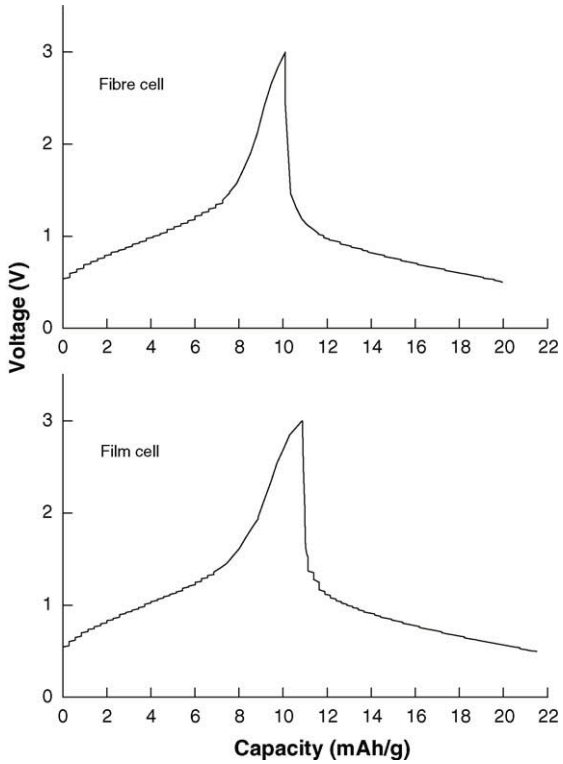


Fig. 6. Charge–discharge curves for fibre cell and film cell of PPy/PF_6|$LiPF_6$–EC–DMC|PPy/PSS; current density = 0.1 mAh cm^{-2}.

Cathode:

$$[PPy^+]\,PF_6^- + e^- \rightarrow [PPy^0] + PF_6^- \quad (2)$$

Charge–discharge curves (10th cycle) for the polymer cells with hollow fibre composite electrodes and for the polymer film electrodes are given in Fig. 6. The open-circuit potentials of both cells are about 0.4 V. Both cells exhibit a coulombic efficiency of nearly 98%. The discharge capacities versus cycle number are presented in Fig. 7. The fibre battery performance is similar to that of the conventional film battery. On the other hand, the fibre battery displays some unique mechanical properties and has the potential for integration into textile structures.

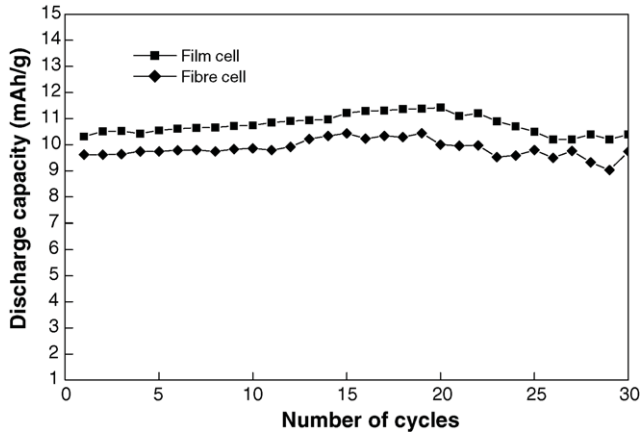


Fig. 7. Discharge capacity vs. cycle number for a fibre cell and a film cell of PPy/PF_6|$LiPF_6$–EC–DMC|PPy/PSS; current density = 0.1 mAh cm^{-2}.

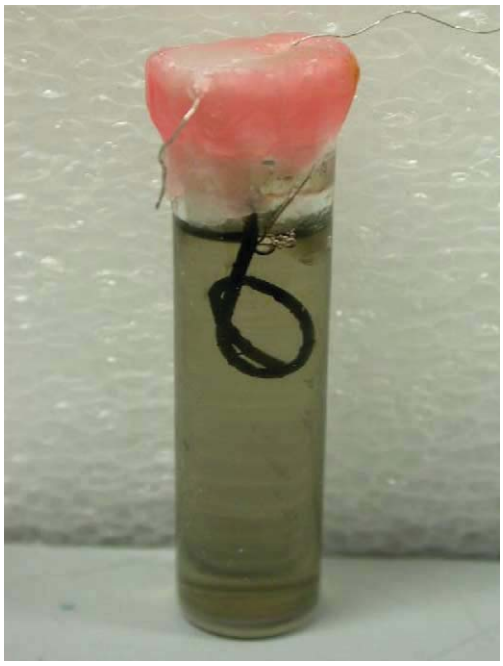


Fig. 8. Photograph of knotted fibre battery.

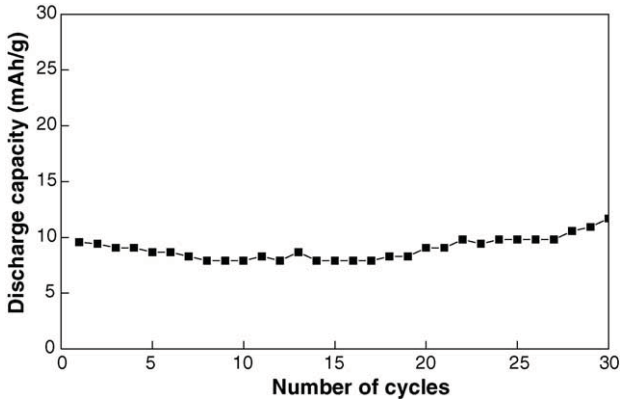


Fig. 9. Discharge capacity vs. cycle number of knotted fibre battery; current density = 0.1 mAh cm^{-2}.

In order to test the flexibility of the fibre electrode, it was tied into a knot, and then sealed in a cell. A cell with knotted electrodes after 100 cycles is shown in Fig. 8. The capacity of the knotted electrode (Fig. 9) is found to be similar to that of an un-knotted electrode (Fig. 7). This indicates that the fibre electrode has very good flexibility.

4. Conclusions

A flexible fibre battery construction that uses conducting polymers as the active material has been evaluated. Capacities of approximately 10 mAh g^{-1} over 30 cycles can be obtained. Although the fibre electrodes have been tested in

flooded cells, fibre batteries with only internal electrolyte are currently being constructed and tested.

Acknowledgements

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